Hydrolysis of Vegetable Oils in Sub- and Supercritical Water

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RESEARCH NOTES

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Water, in its subcritical state, can be used as both a solvent and reactant for the hydrolysis of triglycerides. In this study, soybean, linseed, and coconut oils were successfully and reproducibly hydrolyzed to free fatty acids with water at a density of 0.7 g/mL and temperatures of 260–280 °C. Under these conditions the reaction proceeds quickly, with conversion of greater than 97% after 15–20 min. Some geometric isomerization of the linolenic acids was observed at reaction temperatures as low as 250 °C. Reactions carried out at higher temperatures and pressures, up to the critical point of water, produced either/or degradation, pyrolysis, and polymerization, of the oils and resultant fatty acids.

Introduction

The development of environmentally compatible manufacturing processes, which avoid the use of organic solvent, has become highly desired recently. A review of "green" manufacturing options has just been published (Anastas and Williamson, 1996), including an excellent review on the use of supercritical fluids by Tumas (Morgenstern et al., 1996). Such media avoid many of the objections and problems associated with organic solvents, including flammability, product contamination, and their associated disposal cost. To date, many processes have been conducted in the presence of supercritical carbon dioxide ($SC-CO_2$) due to its low cost, convenient critical properties, and relative inertness, particularly processing products intended for use in the food industry (King and List, 1996).

Supercritical water ($SC-H_2O$) and its subcritical analogue are also receiving increased interest as alternatives to organic solvents (Shaw et al., 1991). The critical properties of $SC-H_2O$ are quite high ($T_c = 374$ °C, $P_c = 218$ atm, and $\rho_c = 0.32$ g/mL) relative to those for $SC-CO_2$. Water has the capability of dissolving both nonpolar and polar solutes since its dielectric constant can be adjusted from a room temperature value of 80 to a value of 5 at its critical point. Therefore, water can solubilize most nonpolar organic compounds including most hydrocarbons and aromatics starting at 200–250 °C and extending to the critical point (Gao, 1993; Connolly, 1966). This property of sub- and $SC-H_2O$ has been exploited since the early 1980s for the destruction of hazardous waste (Modell, 1989) and has been covered in several excellent reviews (Hutcheson and Foster, 1995; Savage et al., 1995). Recently, Hawthorne and co-workers (Yang et al., 1995; Hawthorne et al., 1994) have shown the potential of water as an extraction solvent in analytical chemistry, particularly when applied to the characterization of environmental contaminants in soil matrices. Several studies have been undertaken to explore the use of water in its near-critical or critical state for conducting synthetic organic chemistry. Some of these include the oxidation of alkyl

aromatics (Holliday, 1995), metal-catalyzed organic transformations (Parsons, 1996), the oxidation of methane (Lee and Foster, 1996; Savage et al., 1994) in hydrothermal systems (Katritzky et al., 1995), and the dehydration of alcohols (Xu et al., 1991).

Hydrolysis reactions have been an important option for many years in the processing of oils and fats for the oleochemical industry. These name reactions, such as the Twitchell process (Sonntag, 1979) or Colgate–Emery synthesis (Barnebey and Brown, 1948), of complex mixtures of fatty acids have historically been conducted at low pressures and elevated temperatures, although the Eisenlohr process (Eisenlohr, 1939) was facilitated at pressures approaching 240 atm. It is interesting to note that processes like the Colgate–Emery process are conducted at conditions similar to subcritical water (250 °C and 50 atm), although historically they have not been interpreted in this light because the oil to water ratio is usually 2 to 1, making it more of a steam-based hydrolysis than a subcritical one. For this reason, we have conducted a more fundamental study of the hydrolysis of vegetable oils under sub- and supercritical water conditions where the density is more liquidlike (>0.5 g/mL) than gaslike.

In this research, hydrolytic reaction conditions ranging in temperatures of 250–375 °C have been applied to the hydrolysis of vegetable oils, such as soybean oil, linseed oil, and coconut oil. From the derived data, approximate conversion rates have been estimated and conditions optimized for the production of the derived fatty acids. Analytical characterization of reaction product mixtures has been accomplished by supercritical fluid chromatography (SFC) (Chester, 1996) and gas chromatographic analysis of methyl esters of fatty acids (GC-FAME). The results of these baseline studies are expected to aid in the design of a continuous-flow conversion process employing sub- or supercritical water and to offer an alternative method that might be faster and devoid of catalyst residues for the processing of triglyceride-based fats and oils to their component fatty acid constituents.

Materials and Methods

Vegetable oils used in these experiments were as follows: coconut oil (EDKO 76), PVO Foods, Inc., St.

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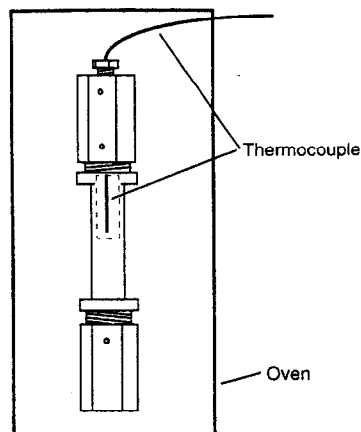
Figure 1. Schematic of the reaction vessel in an oven, showing the placement of the thermocouple inside the vessel.

Table 1. Dependence of Conversion of Triglycerides (>97%) to Fatty Acids on Time and Temperature[a]

oil	reaction time (min)	reaction temperature (°C)
soybean oil (RBD)[b]	20	270
hydrogenated soybean oil	15	280
linseed oil	20	280
	69	260
coconut oil	15	270

[a] The density of water was 0.7 g/mL for data shown. [b] Refined, bleached, deodorized soybean oil.

Louis, MS; hydrogenated soybean oil (17 Stearin), Van Den Bergh Foods Co., Lisle, IL; linseed oil, Minnesota Linseed Oil Co., Minneapolis, MN; soybean oil (refined, bleached, deodorized (RBD)), Archer Daniels Midland, Granite City, IL. Deionized water was used without further purification. The high-pressure batch reaction vessel (Figure 1) consisted of a 316 stainless steel 8-in.-long coned and threaded nipple (1 inch o.d., $^9/_{16}$ in. i.d.) capped at one end and fitted with a $^1/_4$ in.−1 in. 316 SS union at the other end (Autoclave Engineers, Erie, PA). The union was fitted with a $^1/_8$−$^1/_4$ in. thermocouple adaptor in which a thermocouple (Type J, $^1/_8$ in. o.d. Inconel sheath, Omega Engineers, Stamford, CT) was placed such that the tip of the thermocouple was approximately at the halfway point of the nipple. The vessel had an internal volume of 35.5 mL and a pressure rating of 10 000 psi. The thermocouple was connected to a digital readout and/or a chart recorder for an accurate reading of the temperature inside the vessel. The vessel was cooled by two opposing 12 in. air knives (Exair-Knife No. 2012, Exair Corp., Cincinnati, OH).

Supercritical fluid chromatography (SFC) analysis of the reaction products was performed on a Lee Scientific Series 600 SFC (Dionex Corp., Sunnyvale, CA). The SFC unit was equipped with a timed injector (200 nL injection loop), which was held open for 0.5 s, and a Dionex SB-Phenyl-50 capillary column (10 m × 50 μm i.d., 0.25 μm film thickness). The flame ionization detector (FID) was operated at 350 °C, and an integrator (Data Jet-CH$_2$, Spectra-Physics, San Jose, CA) was used for data quantification. The column temperature was held at a constant of 100 °C. The carrier gas was carbon dioxide (SFC/SFE grade, Air Products, Allentown, PA). The column pressure was held at 100 atm for 5 min and then increased to 240 atm at 4 atm/min, followed by an increase to 320 atm at 10 atm/min.

GC-FAME (fatty acid methyl ester) analyses were performed according to previously described methods (House et al., 1994) on a HP5890 Series II GC using a FID detector (Hewlett Packard Co., Wilmington, DE) and a 100% poly[bis(cyanopropyl)siloxane] column (SP-2340, Supelco, Inc., Bellefonte, PA, 60 m × 0.25 mm, 0.20 μm thickness). The GC oven parameters were modified slightly for better separation of the standards. The oven was held at 100 °C for 5 min, then increased to 190 °C at 3 °C/min, then increased at 1 °C/min to 200 °C and held for 15 min, and finally increased at 50 °C/min to 250 °C and held for 1 min for a total time of 62 min. GC-MSD (mass selective detector) analysis of the FAMEs was performed on a HP5890 Series II Plus GC interfaced with a HP5971A MSD using the same column as described above.

In a typical reaction, 25 mL of water and 4 mL of vegetable oil were charged into the high-pressure reaction vessel. The reaction vessel was then placed upright into an oven preheated to approximately 350 °C. The temperature of the reaction was monitored, and the oven was regulated to the desired temperature inside the vessel. The reaction was conducted at this temperature for a specified amount of time. The vessel was then removed from the oven and cooled with the air knives until it was cool to the touch (approximately 10−13 min to reach 35 °C).

Workup of the reaction products usually consisted of pouring the vessel contents into a separatory funnel, adding a small amount of salt (Na$_2$SO$_4$) to the water, and extracting the oil/water mixture with diethyl ether. The ether was then evaporated to leave an oil or a solid consisting of the hydrolyzed fatty acids and any unreacted triglycerides. This extract was then subjected to SFC to determine the degree of hydrolysis. GC-FAME analysis was then utilized to determine if the free fatty acid composition had been altered during the reaction.

Results and Discussion

Approximately 40 reactions were run during the course of this study utilizing the above-described procedures. To determine the parameters for a future continuous flow study, the time versus temperature ratio was studied to find a temperature which did not degrade the oils, in conjunction with a short residence time to optimize the reaction. For these reasons, the majority of the reactions were run for approximately 20 min and in the temperature range of 260−280 °C.

Table 1 tabulates the time and temperatures necessary for at least 97% conversion to free fatty acids based on the SFC analysis. Hydrolysis of these vegetable oils occurred between 15 and 20 min at 270−280 °C and a density of 0.7 g/mL. The coconut oil hydrolyzed the quickest, whereas the linseed oil took the longest. Temperature plays a major role in the time of reaction, as can be seen by the hydrolysis of linseed oil. Lowering the reaction temperature by 20 °C increased the reaction time from 20 to 69 min, with the density remaining consistent in the closed system.

In many of the experiments, the collected water phase came out milky white, indicating an emulsion had formed containing free fatty acids. Hence, sodium sulfate was added to the water to salt-out the fatty acids. Past studies on the hydrolysis of organic esters and ethers, like dibenzyl ether, in water have shown that hydrolysis reactions occur more readily at densities of 0.45 g/mL or higher (Townsend et al., 1989). Consequently, the density for our initial experiments was set at 0.5 g/mL. This produces two phases, liquid and steam, at a density of 0.5 g/mL and 280 °C. To eliminate any ambiguity as to which phase the hydrolysis was occurring in, the density was increased to 0.7 g/mL to ensure that there would be one phase at 270 °C

Table 2. Effect of Time and Temperature on the Distribution of Linolenic Acid Isomers and Degradation of Linseed Oil Shown as Percent of Total Fatty Acid[a]

time (min)	temperature (°C)	ctt, tct[b]	ttc	cct, ctc	tcc	ccc
	unreacted	0	0.2	0	0	54.7
15	270[c]	1.5	8.1	1.9	7.1	33.8
15	280	3.2	10.1	2.8	8.8	26.2
20	280	4.7	10.8	3.3	9.2	21.3
48	260[c]	2.3	9.2	2.2	8.1	29.9
69	260	3.1	9.9	2.5	8.7	26.3

[a] The density of water was 0.7 g/mL. [b] $c = cis$ and $t = trans$. [c] Not totally converted to free fatty acids.

(Rabenau, 1985). A density of 0.7 g/mL is sufficient to favor hydrolysis over pyrolysis and promotes solubilization of any polar intermediates during the hydrolysis.

GC-FAME analysis was performed on all samples to determine if any degradation occurred to the fatty acids during hydrolysis. Saturated acids, such as caproic, caprylic, capric, lauric, myristic, palmitic, and stearic acids, were stable at temperatures below 300 °C. The unsaturated fatty acids, oleic and linoleic acid, were also relatively unaffected at these same temperatures. However, linolenic acid levels were consistently reduced under these conditions, due to isomerization and degradation. For most reactions, approximately 90% of the linolenic acid was still present, but only 40–60% of the linolenic acid was in the original *cis,cis,cis* isomer form. The variation in this conversion proved to be dependent on time and temperature. Hydrolysis conducted at higher temperatures or longer reaction times produced less of the *cis,cis,cis* fatty acid (see Table 2). From Table 2, it can also be seen that the *trans,trans,cis* and *trans,-cis,cis* isomers are present, and each represents 10–11% of the product composition after hydrolysis. This isomerization occurred even at 250 °C, although not to as a great an extent as seen at 270–280 °C. It is also interesting to note that the *all-trans* isomer is not formed in any significant amount. The isomer distribution patterns were found to be consistent during the course of these studies. Linoleic acid, with two double bonds, did not undergo any detectable amount of geometric isomerization.

Several reactions were also performed at higher temperatures to see the effect on the oils. The RBD soybean oil was subjected to subcritical temperatures of 300 °C for 11 and 25 min and 320 °C for 13 min. The same oil was also processed at a supercritical temperature of 375 °C for 8 min. These reactions yielded a very dark brown oil which was only partially soluble in ether and hexane. GC-FAME analysis indicated severe decomposition, pyrolysis, or polymerization, of the fatty acids, which was consistent with the color and nature of the resultant reaction mixture. Hydrogenated soybean oil exposed to the same conditions, also showed this onset of severe thermal degradation.

Conclusion

The use of subcritical water at high densities has proven to be an effective means of hydrolyzing vegetable oils to free fatty acids. Hydrolysis occurs rapidly, usually within 15–20 min, yielding 97% or better conversion. Supercritical water conditions tended to thermally degrade the reactants and products. Further research is being conducted to design and implement a continuous-flow reaction system based on these studies.

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